C S P

The DOE Center of Excellence for the Synthesis and Processing of Advanced Materials

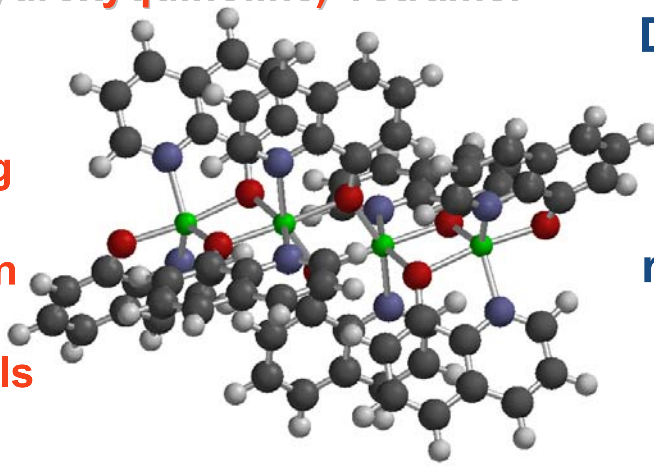
Basic Energy Sciences
Division of Materials
Sciences and Engineering

Smart Materials Based on Electroactive Polymers

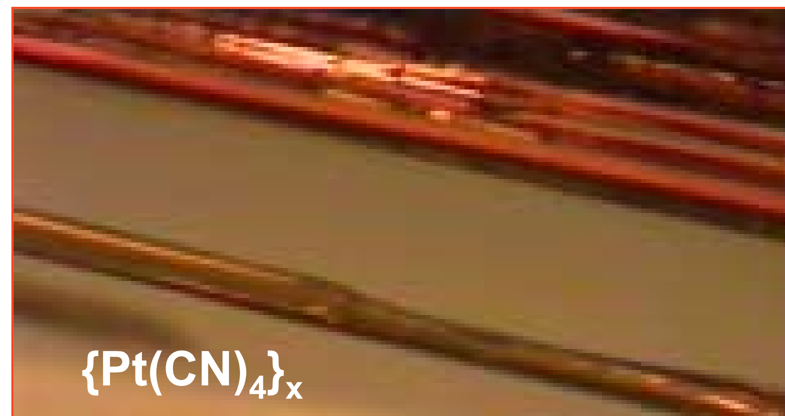
Greg Exarhos, Coordinator, PNNL

Zn (II) bis(8-hydroxyquinoline) Tetramer

A model oligomer for understanding the energy transformation process in OLED materials



Design and synthesize functionalized molecules that self-assemble into predicted hierarchical architectures and that show a predetermined and reversible response to applied stress



Platinum Molecular Wires from Electrochemical Polymerization

>>> Topical Areas Addressed <<<

Precursor Synthesis / Processing

Self-Assembly and Templating

Patterned Architecture Formation

Chemical Surface Modification

Directed Phase Transformations

Structure/Property Relationships

Office of Science
U.S. DEPARTMENT OF ENERGY

Design, Synthesize, and Characterize Polymer Materials Containing Engineered Smartness

- What phenomena are exploited to impart "smartness" ?
  - Volume change as a function of pH, ionicity, temperature
  - Refractive index change with temperature, light intensity
  - Second-order structural transformations (order - disorder)
- How is modeling used to drive materials development ?
- What are controlling factors that promote self-assembly ?
  - Resident chemistry (hydrophobicity, hydrophilicity, hydrogen bonding)
  - Molecular confinement, interconnected porosity
- How are hierarchically-ordered materials characterized ?
  - Beam techniques, magnetic resonance, optical measurements
- How are such materials modified to impart functionality ?
  - Chemical, structural modification
- What physical properties do modified materials exhibit ?
- How are resources marshaled to promote the research ?

Research Distributed Between Two Tasks

- Chemically and Structurally Modified Polymer Composites
  - Copolymers
  - Self-Assembly
  - Characterization
  - Surface Modification
  - Electro-Optic Properties
  - Role of water in phase stability

Pacific Northwest National Laboratory

Oak Ridge National Laboratory

Argonne

Brookhaven National Laboratory

INEEL

- Void Composite Materials with Interconnected Porosity
  - Polymer Dendrimer Synthesis
  - Colloidal Processing Routes
  - Electro-Optic Properties
  - Characterization

Los Alamos National Laboratory

Illinois
University of Illinois at Urbana-Champaign

Pacific Northwest National Laboratory

Chemically and Structurally Modified Co-Polymer Composites

ORNL, ANL, PNNL, BNL INEEL, SNL

Innovative Synthesis and Processing methods impart tailored physical and chemical structure to self-assembled structures that exhibit predicted properties

- **Goals**
  - Understand fundamental inter- and intra-molecular interactions that guide the self-assembly process
  - Understand the response of derived materials to variations in temperature, pressure, solvent composition, constituents
  - Characterize structure and chemistry over variable length scales
- **Ongoing Issues**
  - Can inorganic co-polymers spontaneously order?
  - How are copolymers made multifunctional?
  - Can materials that form crystalline phases undergo ordering phenomena in the presence of a surfactant?

Designer Nanoscale Materials from Self-Assembly of Co-Polymers

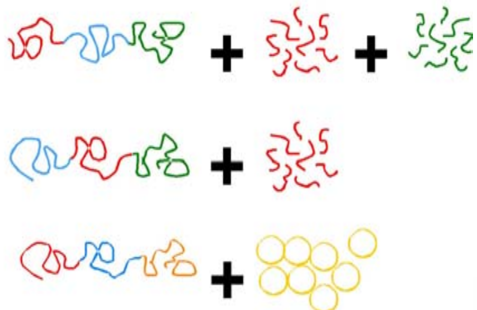
(Manipulation of the Phase Diagram)

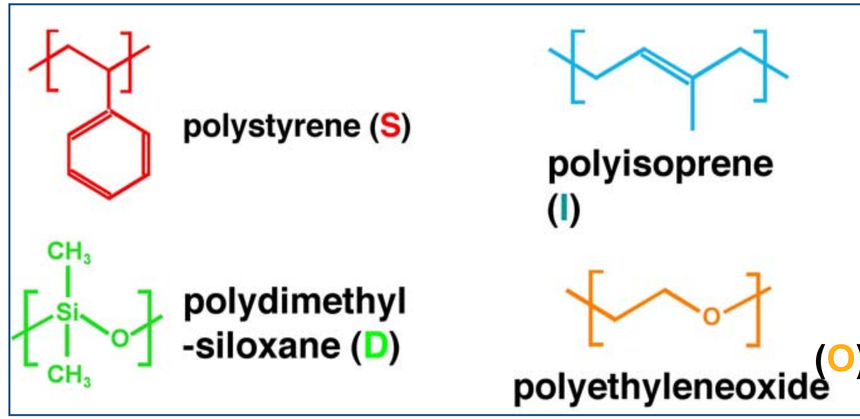
Molecular-Level Mixing of Constituents

SID + S + D

ISD + S

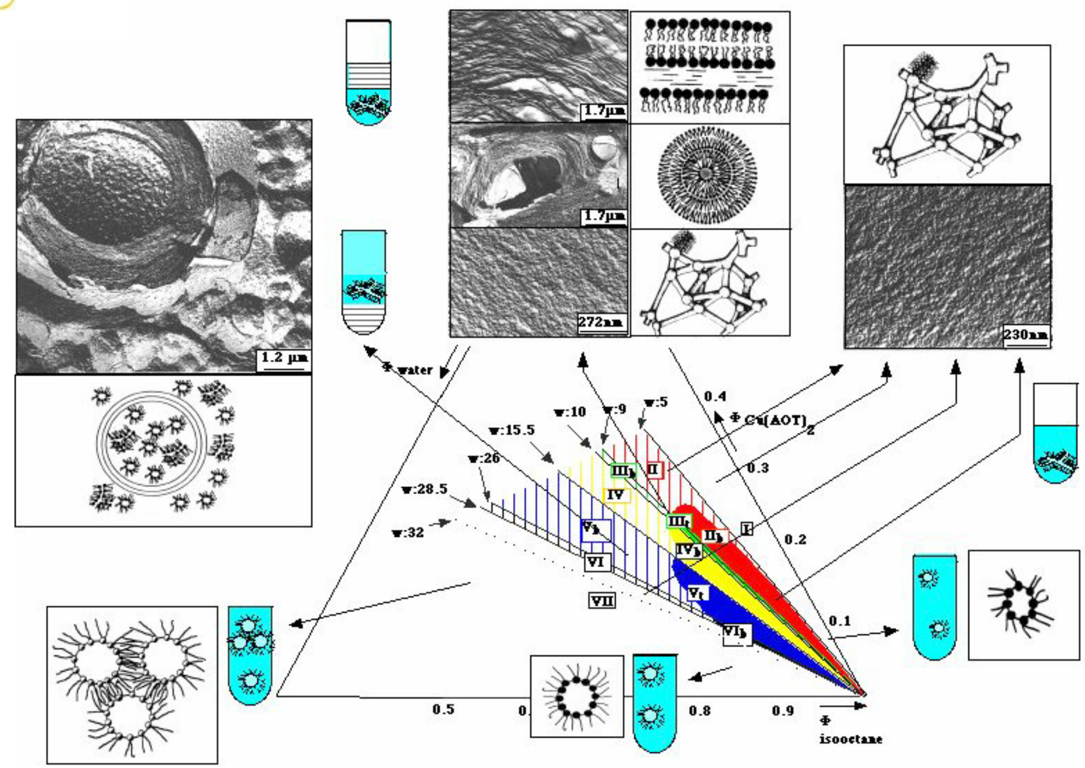
SIO + lithium salt





Approach

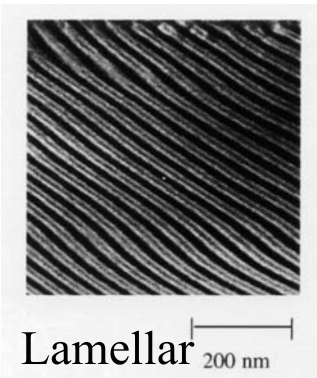
- Blend homopolymers with block copolymers, investigate ion doping, and addition of H_2O
- Characterize changes in morphology
- Seek methods to stabilize the gyroid structure
  - Nanoscopically isotropic
  - Mesoscopically continuous



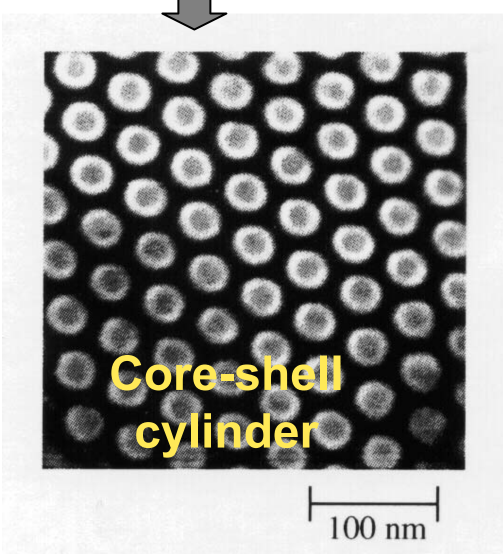
Addition of homopolymer drives triblock of *fixed* composition through several morphologies

Homopolymer addition

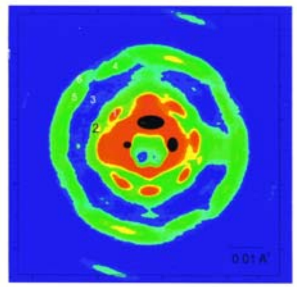
ISD + 15% S



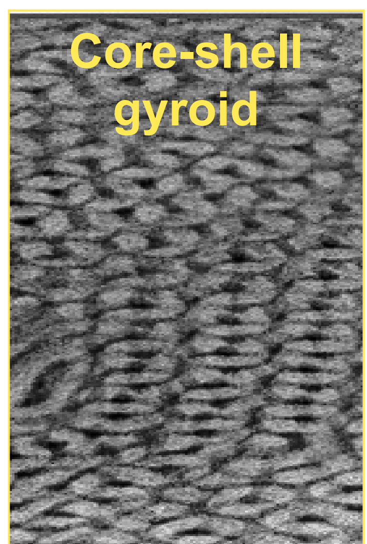
Lamellar



SID + S + D

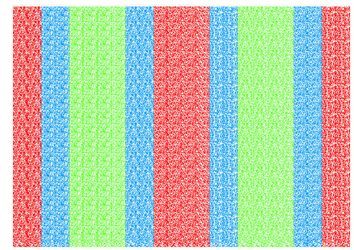


Hexagonal



Sequence effects

SID + ISD



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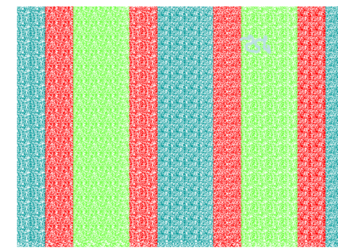
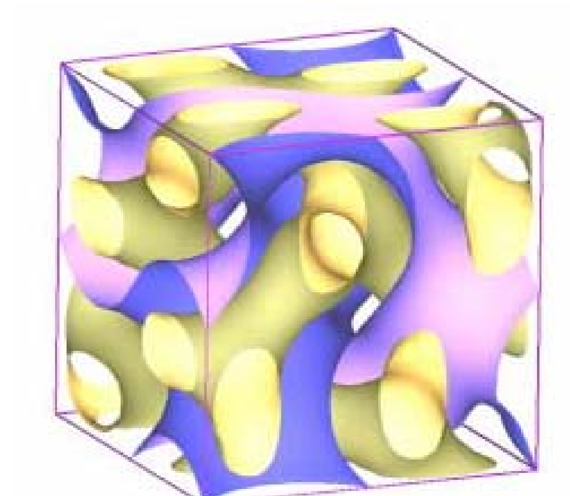


Lamellar



Gyroid

Characterization Tools

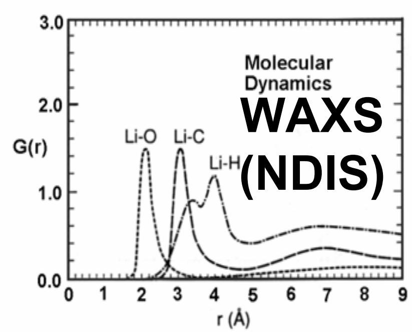
Now and in the Future

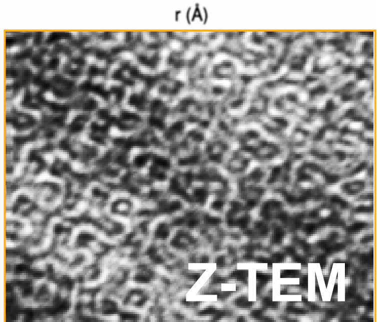
SANS

ODT in ISD1

SAXS

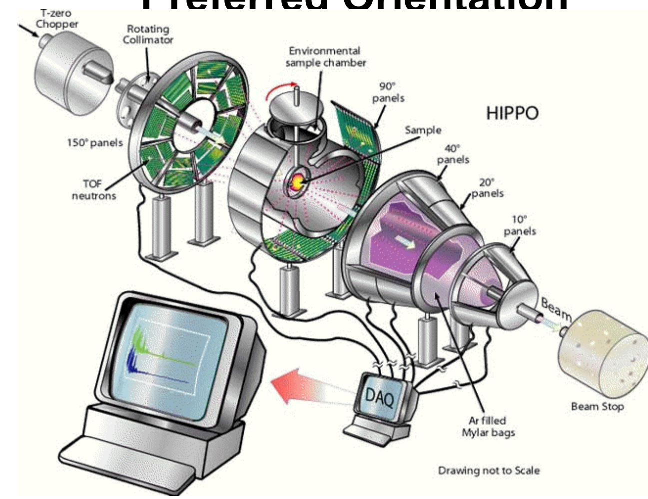
Lamellar morphology in ISD





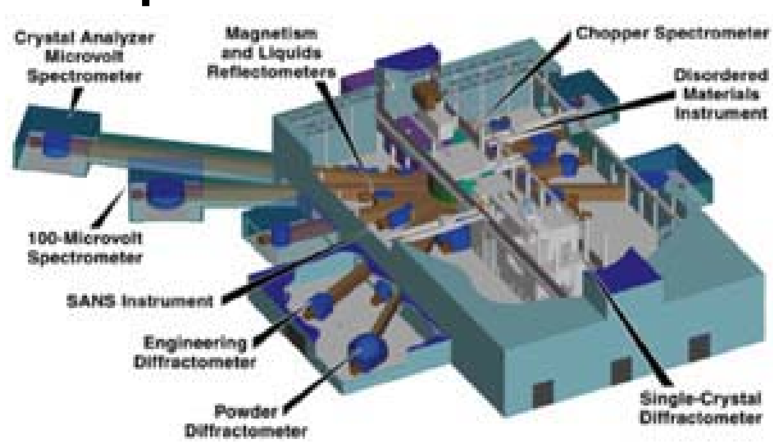
- New Wide Angle Neutron Scattering Instrument at LANSCE
- LBNL, LANL, SNL, ORNL interaction
- Wide range of P and T
- Research applications: Texture/stress, chrystallography, **liquids and amorphous materials**, time-resolved studies

HIPPO – High Pressure Preferred Orientation

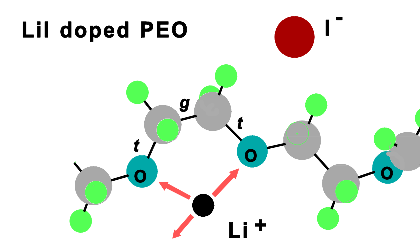


Liquids and Disordered Materials Diffractometer

proposed SNS facility



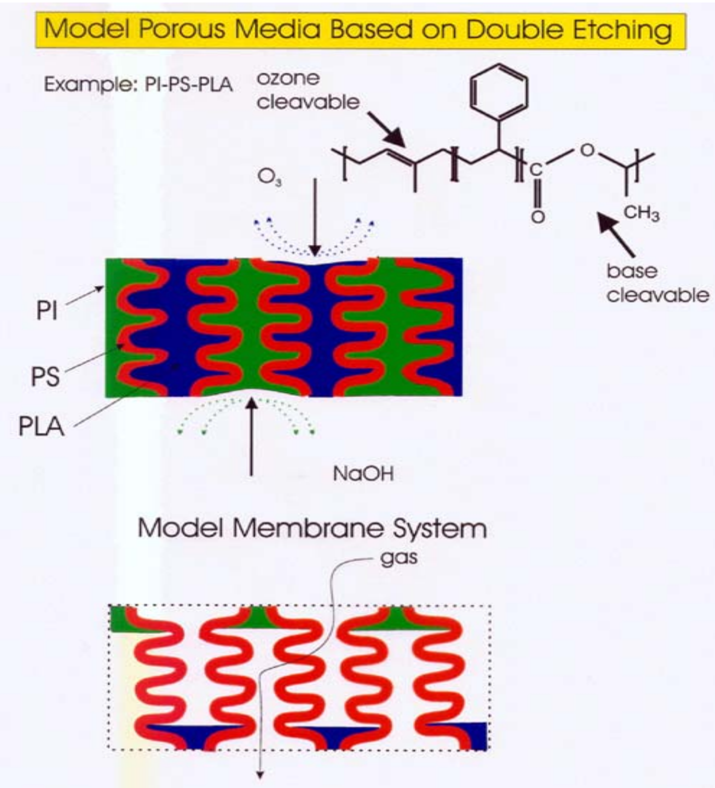
For the study of soft materials:low density fluids, liquids, melts, solutions, glasses, polymers, amorphous materials, and semicrystalline solids.



Local structure of LiI doped PEO from Neutron Diffraction Isotopic Substitution (NDIS) method.

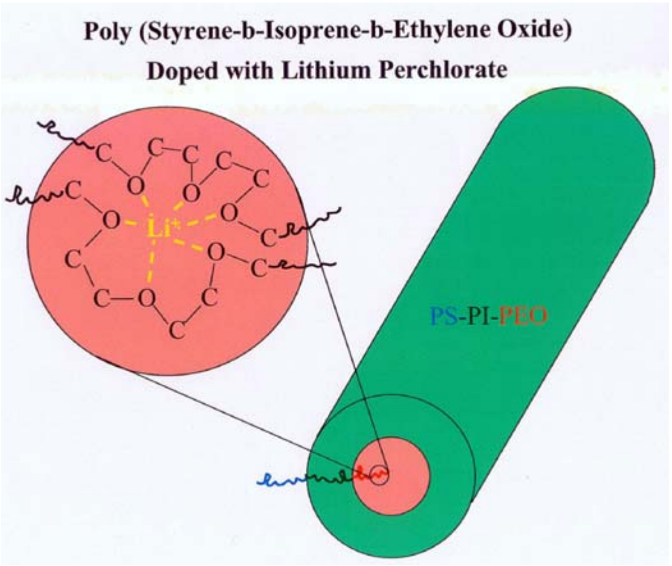
Some Selected Applications

Gas separation membranes based on double etching of gyroid phase - Leverages gas membrane research activity at INEEL



Morphology is controlled by the total copolymer length (MW), the pair-wise interaction parameters (χ_{ij}), and the relative block lengths.

Ion conducting membranes based on Li^+ doped SIO for fuel cell applications - Leverages ion-conducting electrode activity at BNL

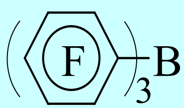


Addition of a constituent homo-polymer expands the stability window of a given morphology without altering block composition.

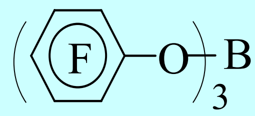
A core-shell gyroid structure is isotropic and continuous, but only exists over a small composition range. Semi-permeable membranes are made without macroscopic alignment of the morphology.

Chemical Modification of ion Transport Membranes for Battery and Sequestration Applications

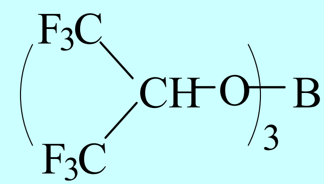
Understand the microscopic origin of electro-responsive phenomena in polymer electrolytes and use the information to synthesize new ion conductors and redox polymers with improved properties



Tris(pentafluorophenyl) borane
(TPFPB)

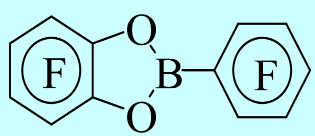


Tris(pentafluorophenyl) borate
(TFPBO)

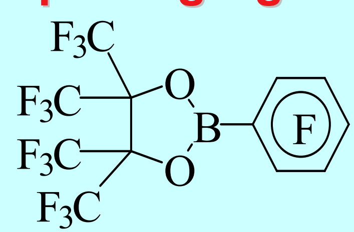


Tris(2H-hexafluoroisopropyl) bo
(THFPBO)

Borane, Borate, and Boronate Anion Complexing Agents



2-pentafluorophenyl-tetrafluoro
-1,3,2-benzodioxaborole
(PFTFBO)



2-pentafluorophenyl-4,4,5,5-tetrakis(trifluorome
-1,3,2-dioxaborole
(PFTFOB)

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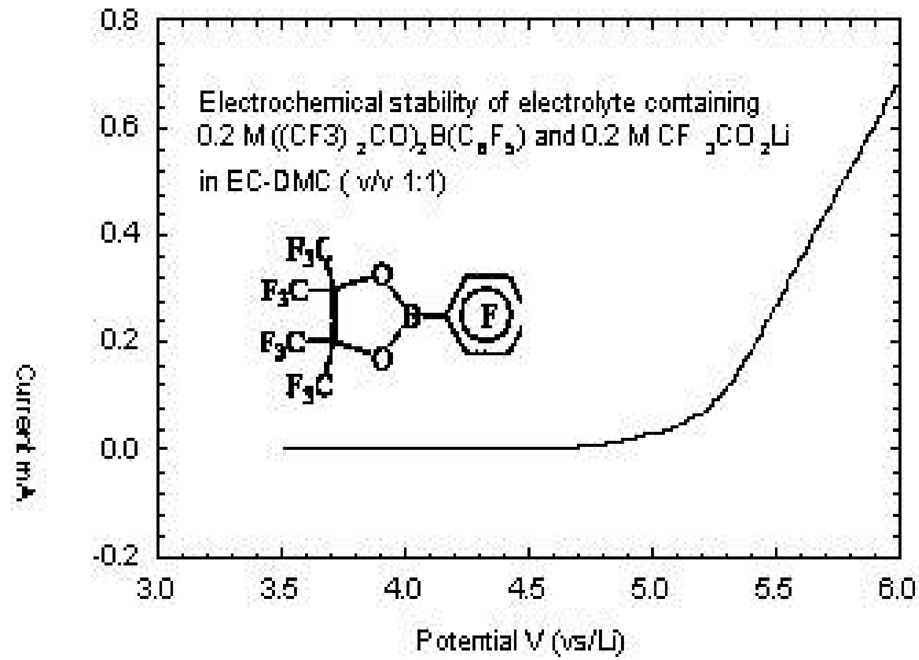
Ongoing Research Activities

- New approach to non-aqueous electrolytes based on Lewis acids instead of Lewis bases.
- Anion complexing agents synthesized with exceptional electrochemical robustness and incorporated into polymer electrolyte
- Selected agents increase LiF solubility over 5 orders of magnitude in non-aqueous solvents
- LiF based electrolytes are compatible with $LiMn_2O_4$ electrodes for battery operation at high temperature

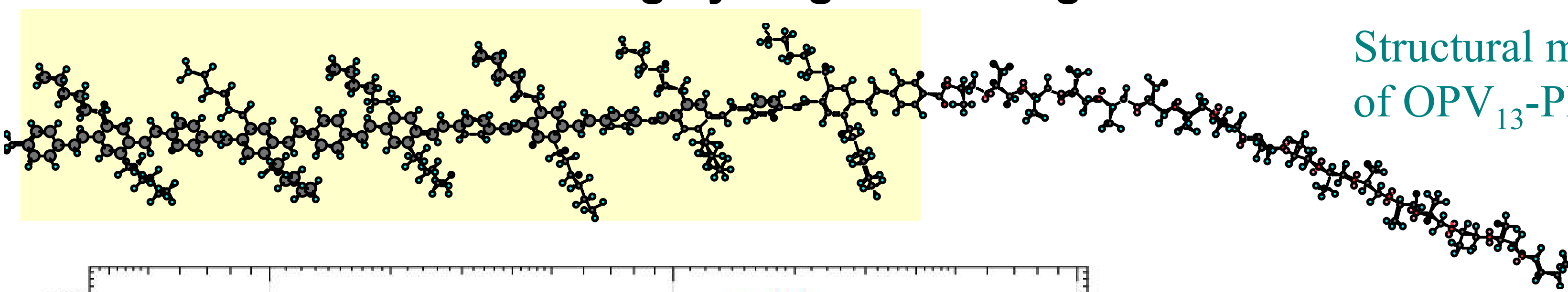


Boronates have greater electrochemical stability than borates

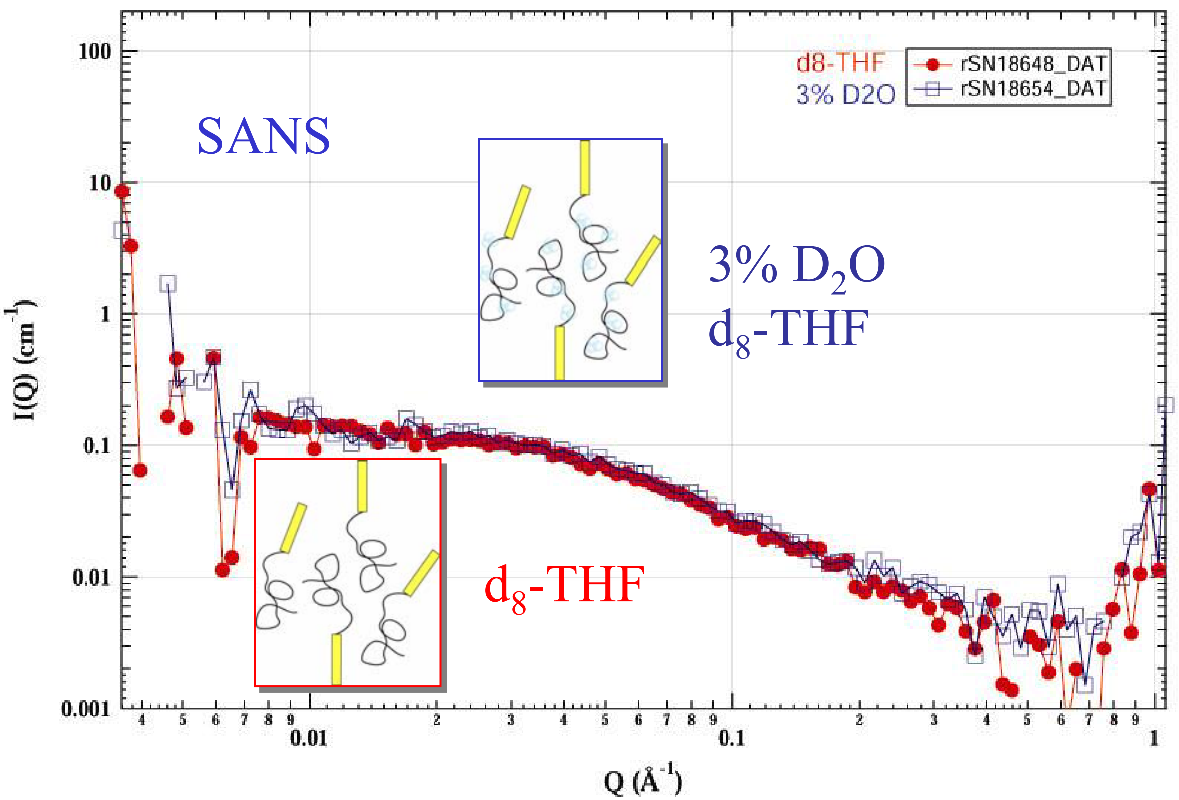
Integrate improved polymer electrolytes with block copolymers to produce structured electrolytes that promote ion transport

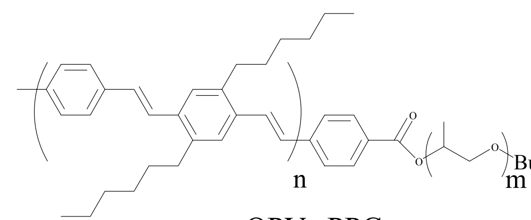
Self Assembly of OPV_{13}-PPG_{70} in D_2O/d_8-THF

Water additions demonstrate the ubiquitous nature of structure-directing hydrogen bonding interactions



Structural model of OPV_{13}-PPG_{16}





OPV$_n$-PPG$_m$

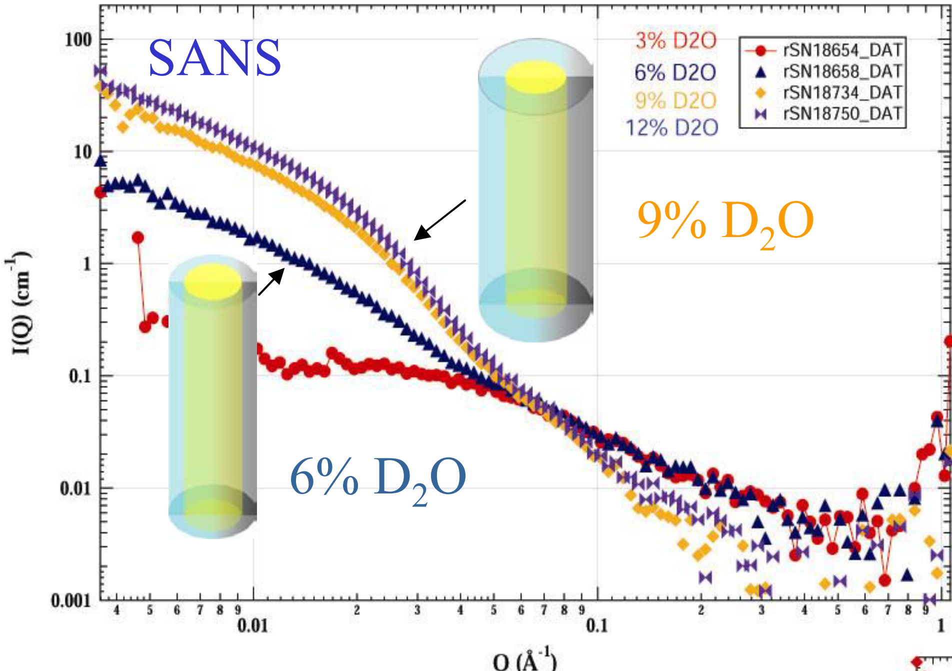
OPV13-PPG70

In THF and 3% D_2O/THF,

No micelle formation,

No aggregation.

Self Assembly of OPV_{13}-PPG_{70} in D_2O/d_8-THF



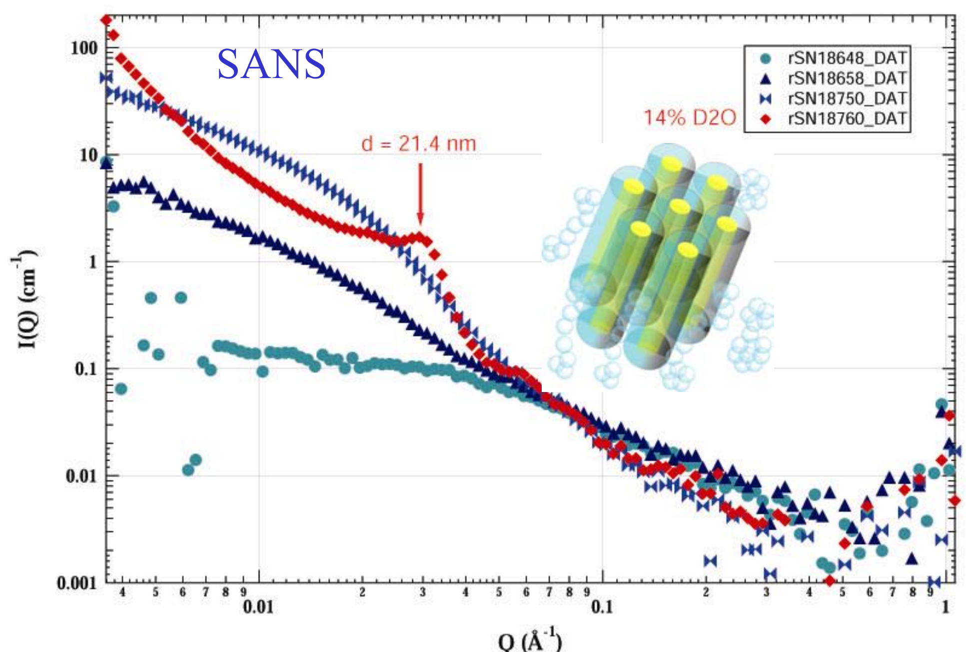
OPV13-PPG70

At 6% water, rod-like micelles formed through self assembly.

6% D_2O r = 7.3 nm
9% D_2O r = 9.0 nm
12% D_2O r = 9.1 nm

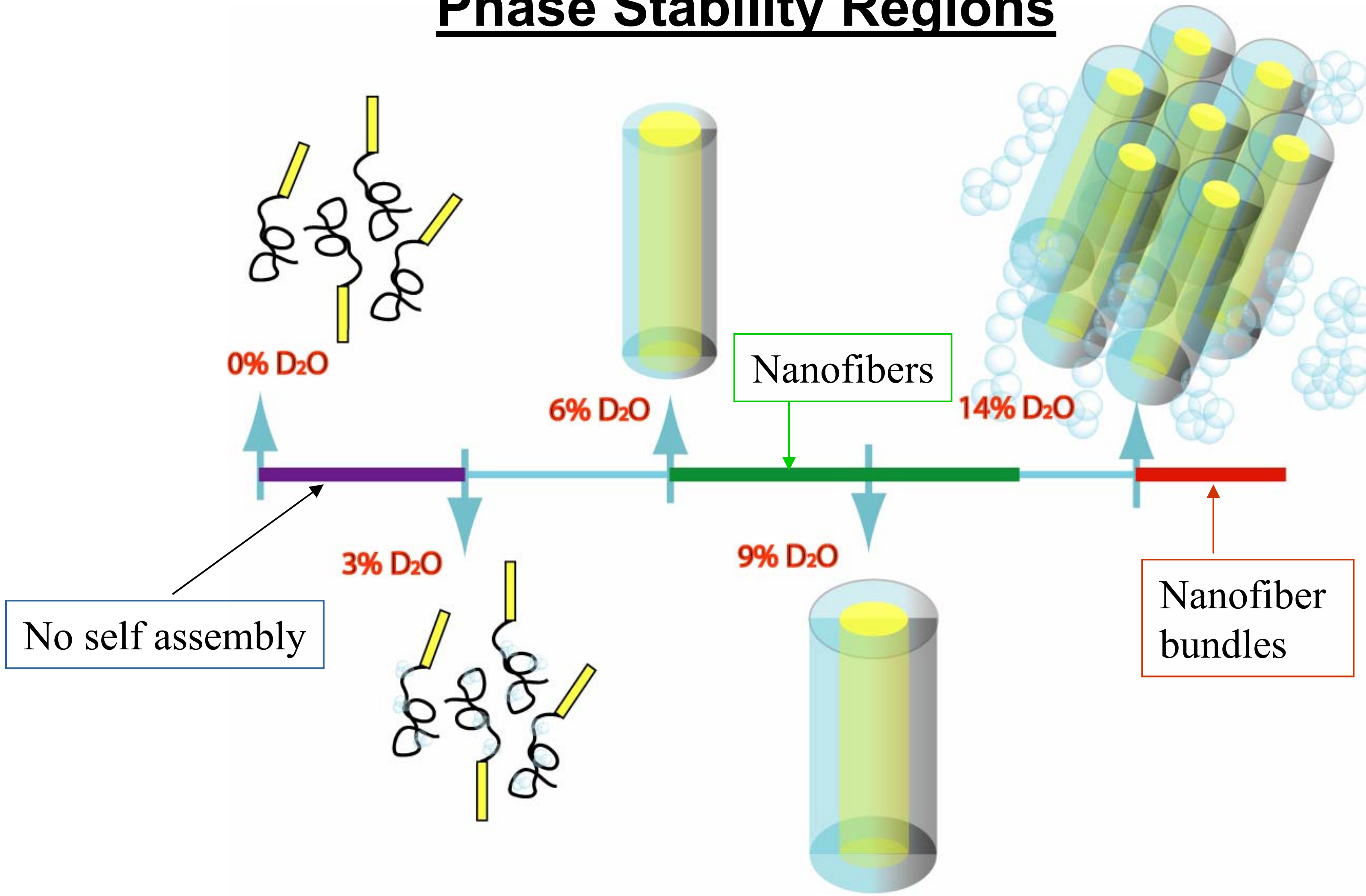
OPV13-PPG70

At 14% D_2O, nanofibers self-assemble into ordered rod bundles.

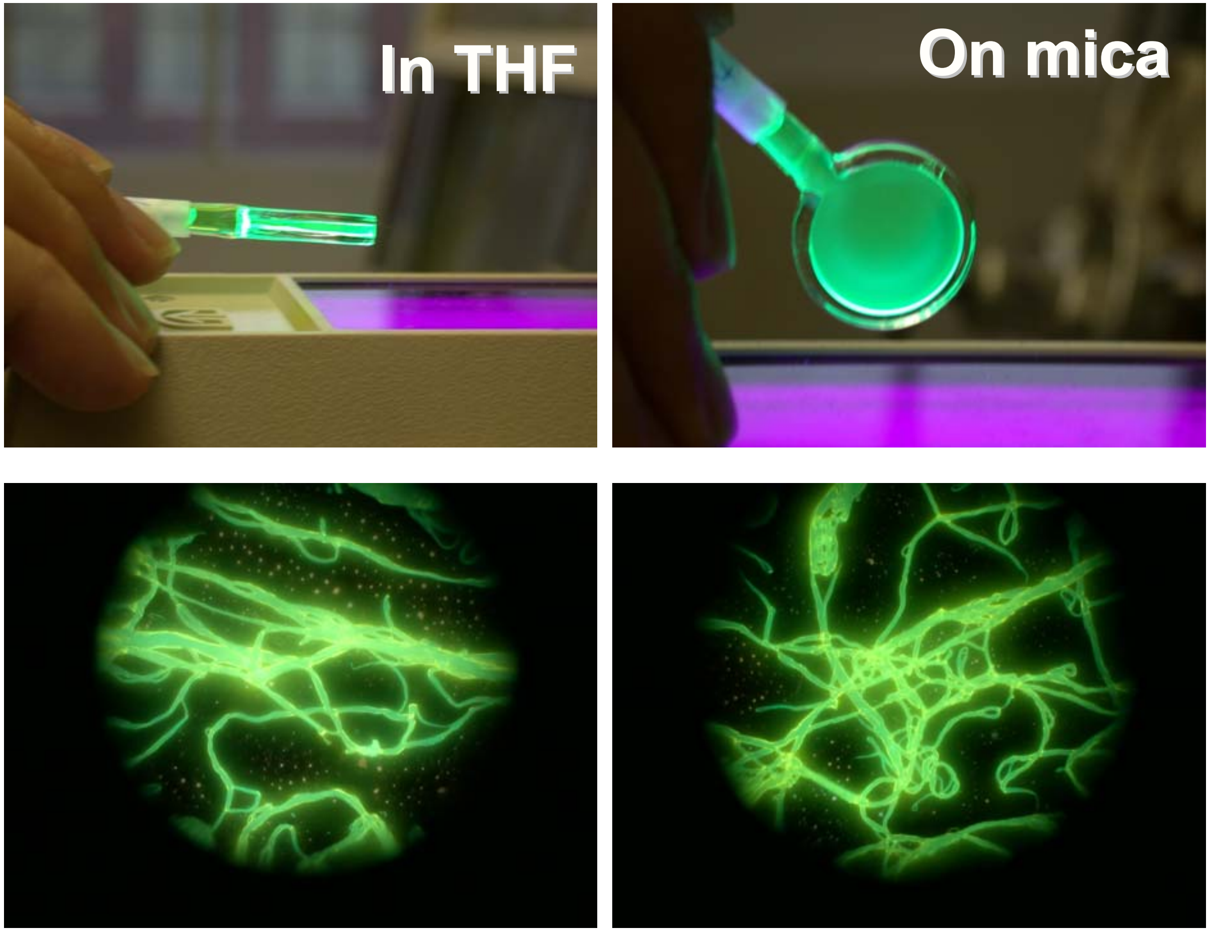


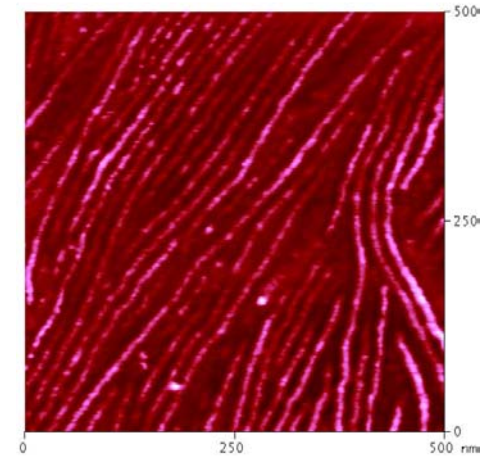
OPV_{13}-PPG_{70} in THF

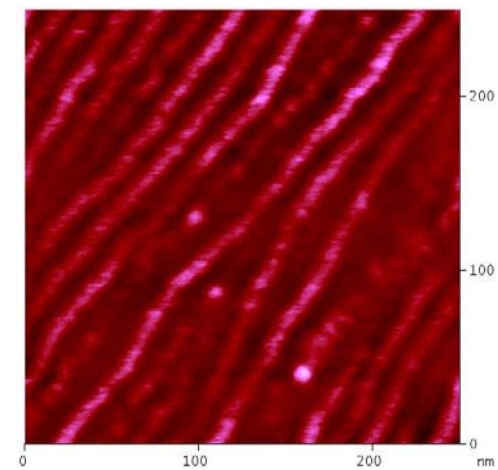
Phase Stability Regions



OPV_{13}-PPG_{70} in THF and on Mica







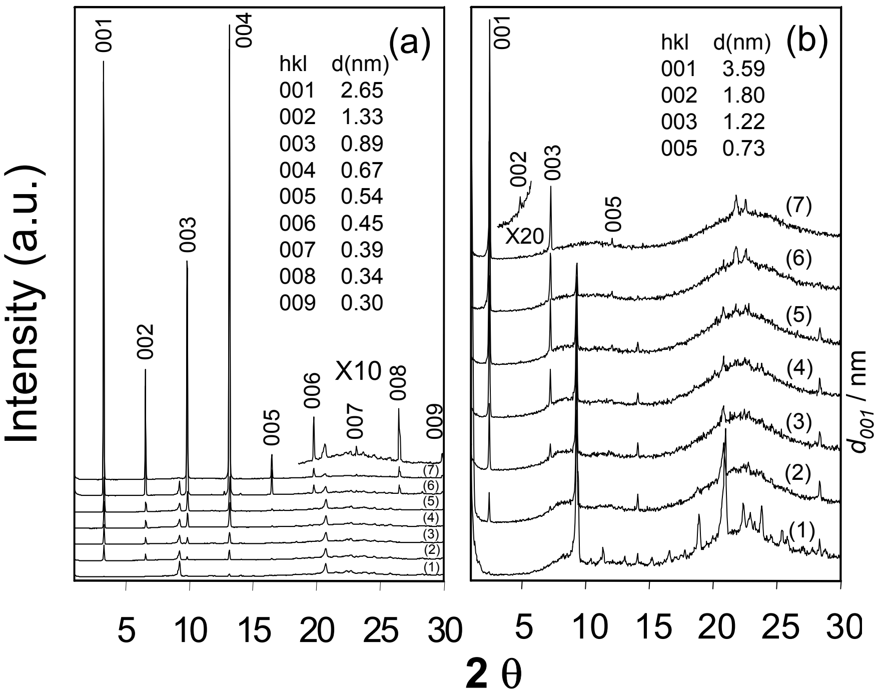
Fluorescence micrographs of OPV_{13}-PPG_{70} fiber bundles

Typical fiber width, of 17.6 nm from AFM measurements, is in good agreement with results (18 nm) from small angle neutron scattering.

Tapping mode AFM measurements of OPV_{13}-PPG_{70} cast from 14% D_2O/THF s onto mica showing nearly aligned individual nanofibers

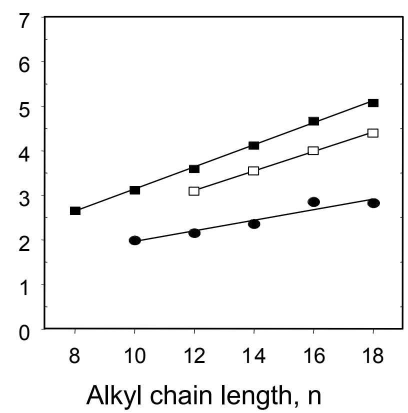
Induced Molecular Self-Assembly in Salt Surfactant Mixtures upon Water Adsorption

Cooled melts of quaternary ammonium salts and amine-based surfactants adsorb water from ambient air. Water localizes at the micelle head group interface in monolayer coverage that creates ordering of surfactant chains.

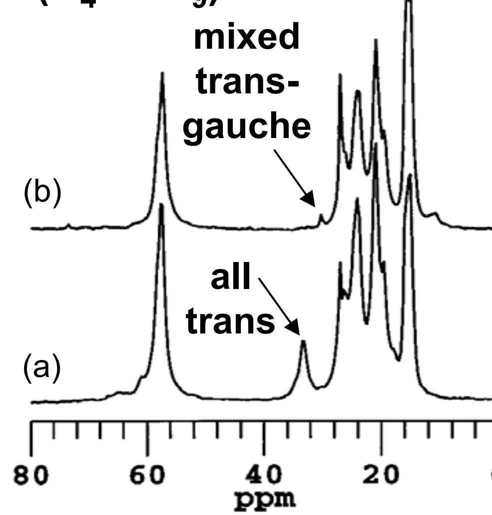


X-ray powder diffraction patterns of C_{16}TMAB/TBAAc and $C_{12}NH_2$/TBAAc mixtures acquired under ambient conditions as a function of time.

Variation in the basal spacing of C_nTMAB/TBAAc and C_nNH_2/TBAAc



^{13}C MAS NMR probes interior methylene carbon (C_4 to C_9) conformation



Alkyl-trimethylammonium surfactants form ordered monolayers, while alkylamines form less ordered bilayers resulting from intermolecular hydrogen bonding with monolayer water coverage.

Void Composite Materials with Interconnected Porosity

PNNL, UI/MRL, LANL, LLNL, NRC

Molecular self-assembly approaches are used to synthesize porous nanocomposites to promote molecular transport; NMR approaches to characterize pore channels augment beam techniques that probe structure at larger distances.

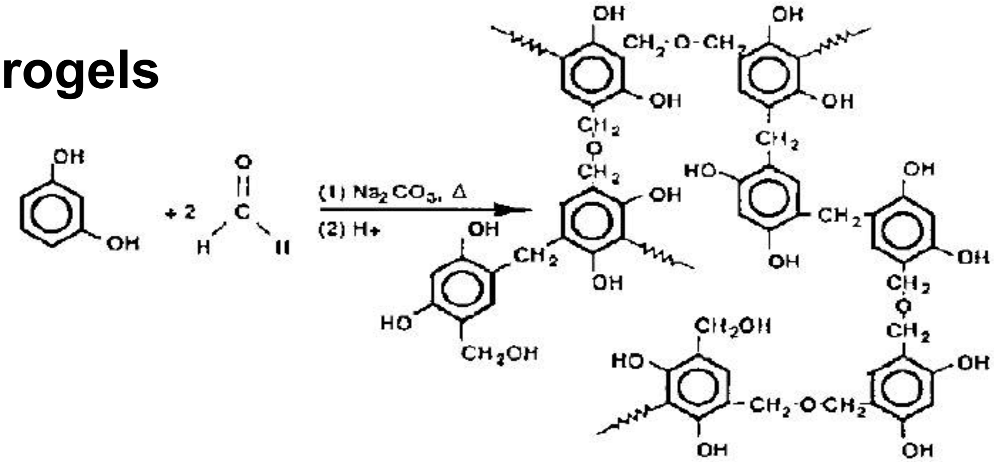
- **Goals**
  - **Understand the catalyst role in promoting network connectivity**
  - **Understand the response of derived materials to variations in temperature, pressure, solvent composition, constituents**
  - **Characterize structure and chemistry over variable length scales**
    - **^{13}C NMR methods probe processing effects on framework rigidity**
    - **^{129}Xe methods probe pore interconnectivity**
- **Ongoing Issues**
  - **How does chemical nature of the crosslink influence flexibility/rigidity?**
  - **How is the relative amount of mesoporosity to nanoporosity determined?**

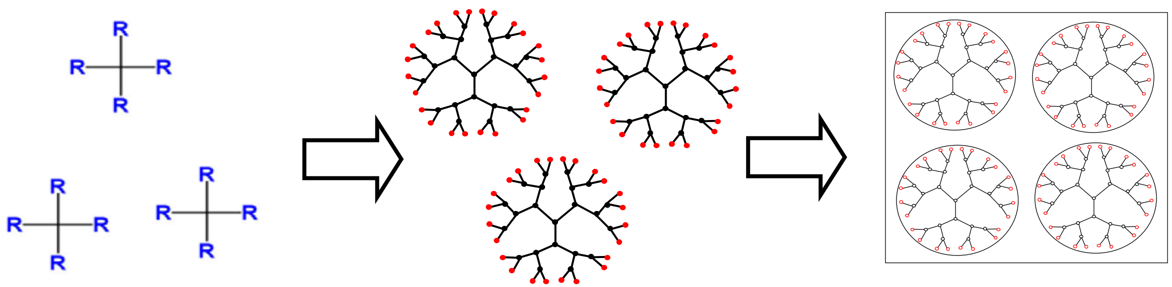
70 nm

Tailored Nanoscale Pore Architectures

Dendrimer-Based Aerogels

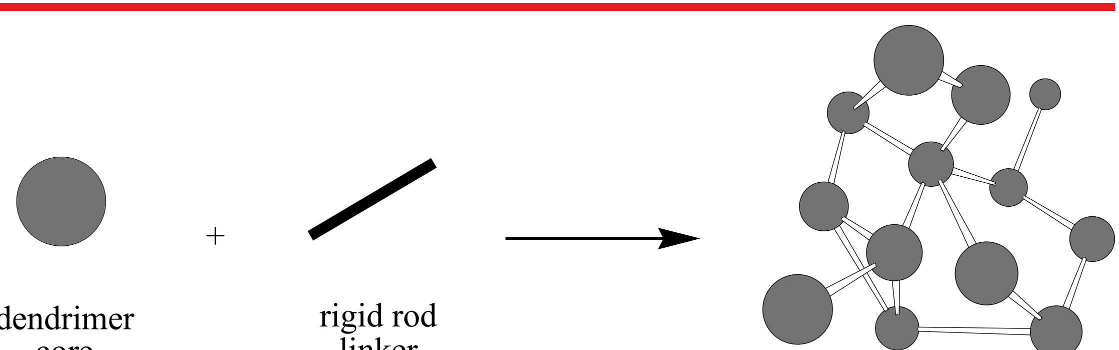
Catalyzed (C) polymerization of resorcinol (R) formaldehyde (F) precursors leads to low density aerogel formation





Organic aerogels from dendrimers (level 1 porosity)

Organic aerogels with rigid rod spacers (level 2 porosity)



dendrimer core

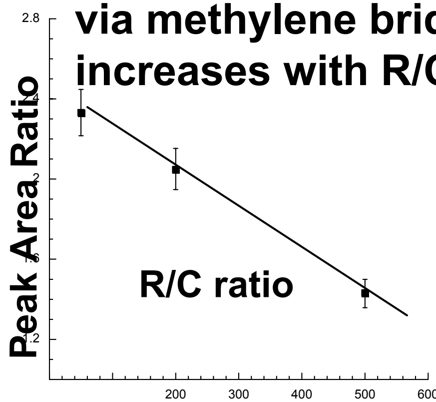
rigid rod linker

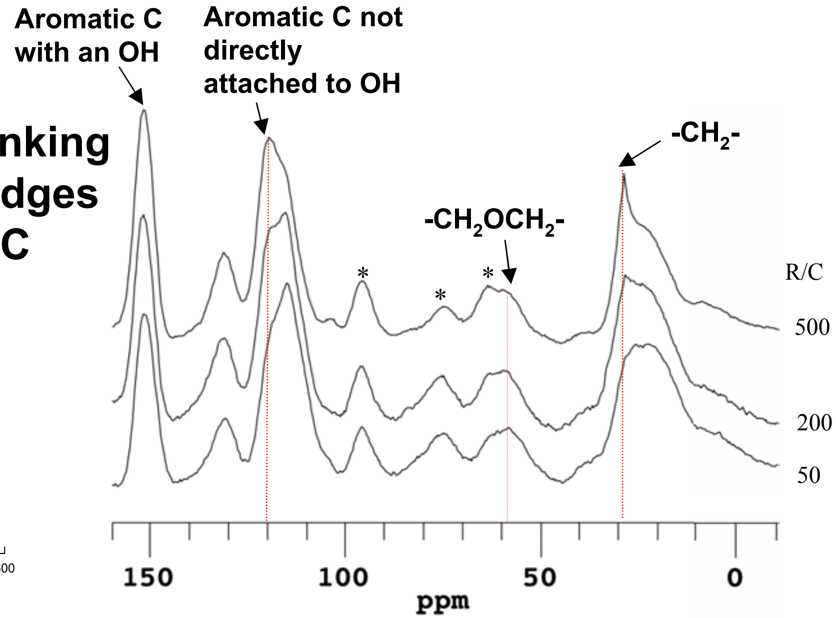
3-D "scaffold" low-density network

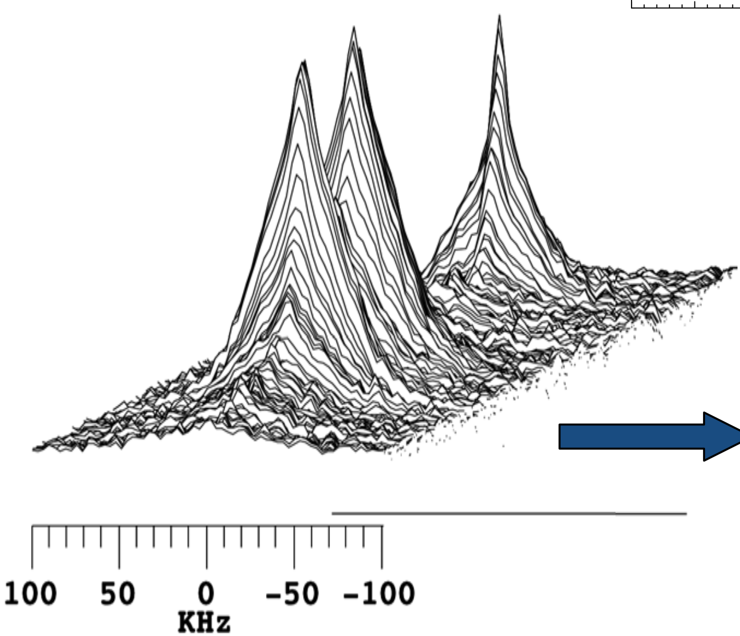
Solid State ^{13}C NMR Methods Probe Degree of Crosslinking in Aerogels as a Function of Catalyst / Precursor Ratio

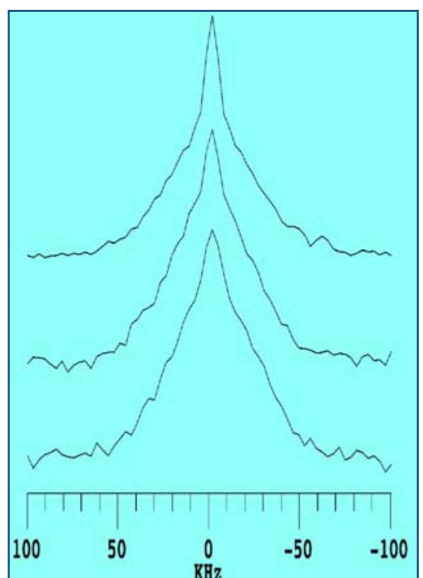
Relate processing parameters to network rigidity

Degree of crosslinking via methylene bridges increases with R/C





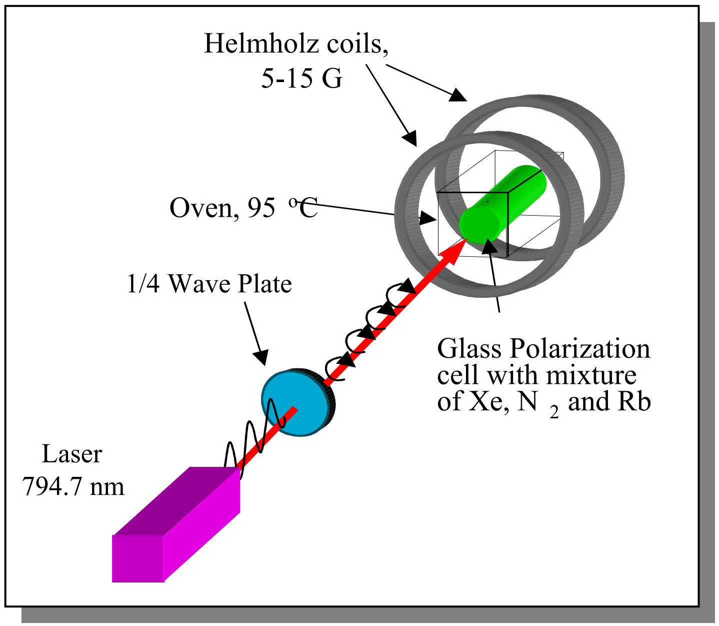




2D WISE ^{13}C solid-state NMR measurements indicate that the probe atoms exhibit a higher degree of mobility for samples prepared with higher R/C ratios due to fewer crosslinks.

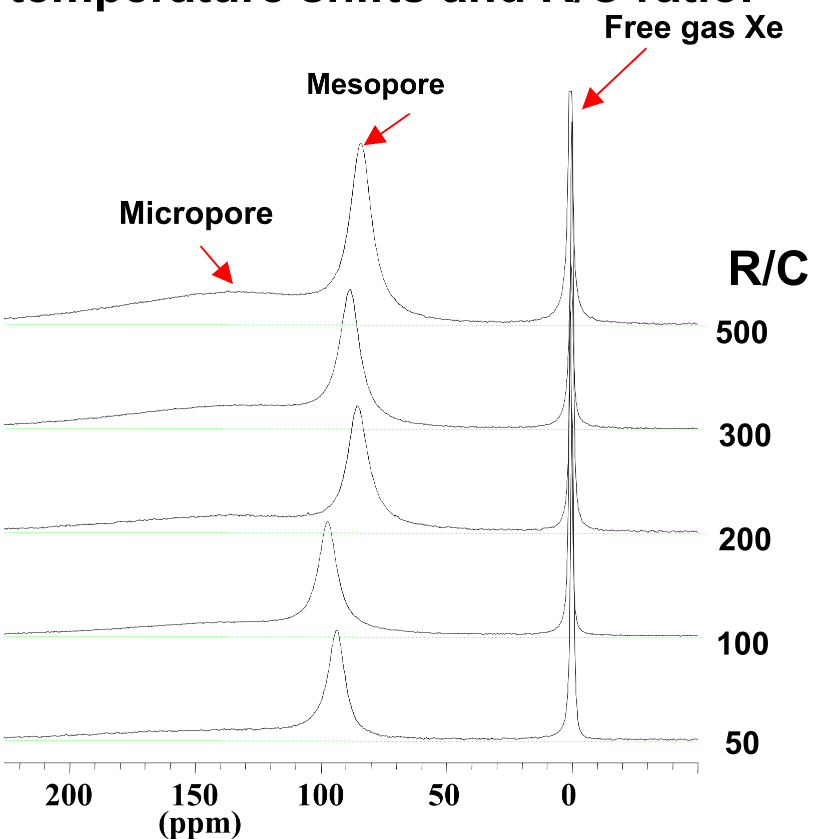
HP ^{129}Xe NMR Spectroscopy Probes Nanopore Size and Connectivity at the Molecular level

HP ^{129}Xe NMR produced by optical pumping (enhancement of the ^{129}Xe signal by several orders of magnitude)

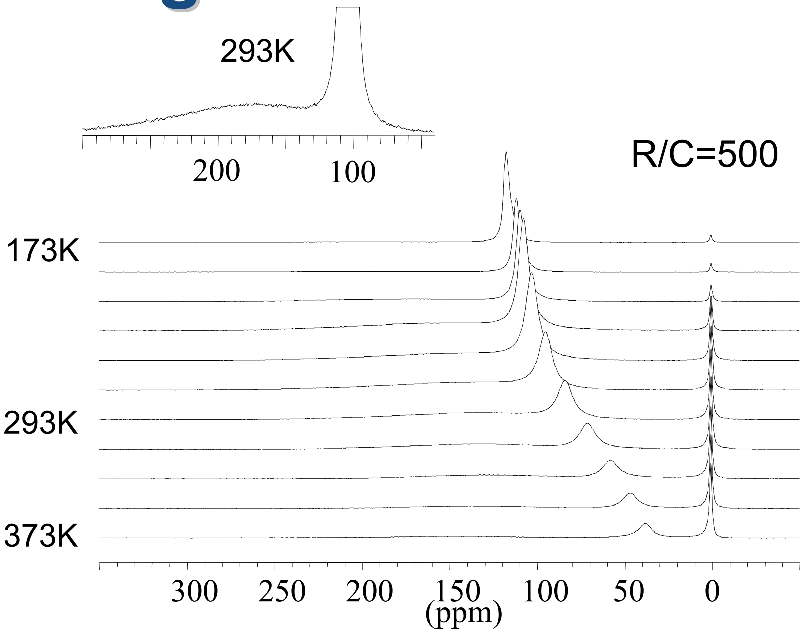


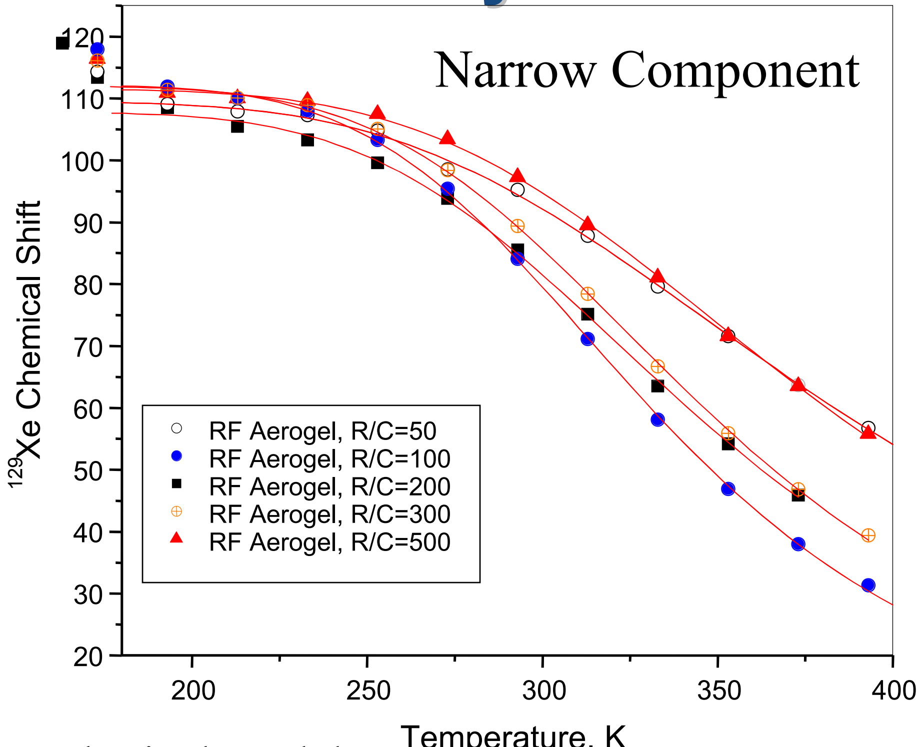
Spin polarized xenon vapor percolates through the interconnected porosity; the ^{129}Xe line exhibits a chemical shift and line broadening that change with the nature and size of the pores.

CF ^{129}Xe NMR spectra for RFA with different R/C show two signals of various width and intensity. No apparent correlation was found between the observed room temperature shifts and R/C ratio.

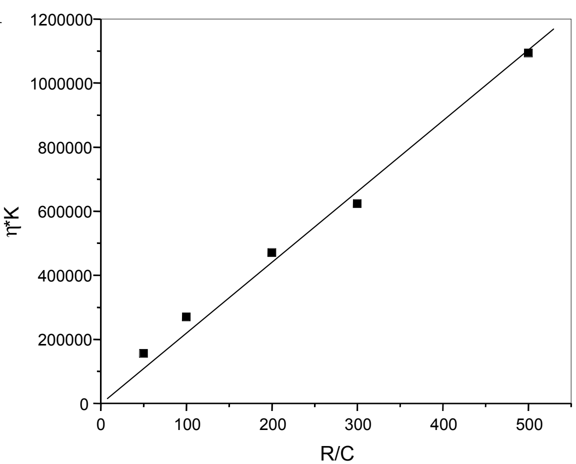


Variable Temperature CF ^{129}Xe NMR in Resorcinol Aerogels Probes Pore Interconnectivity



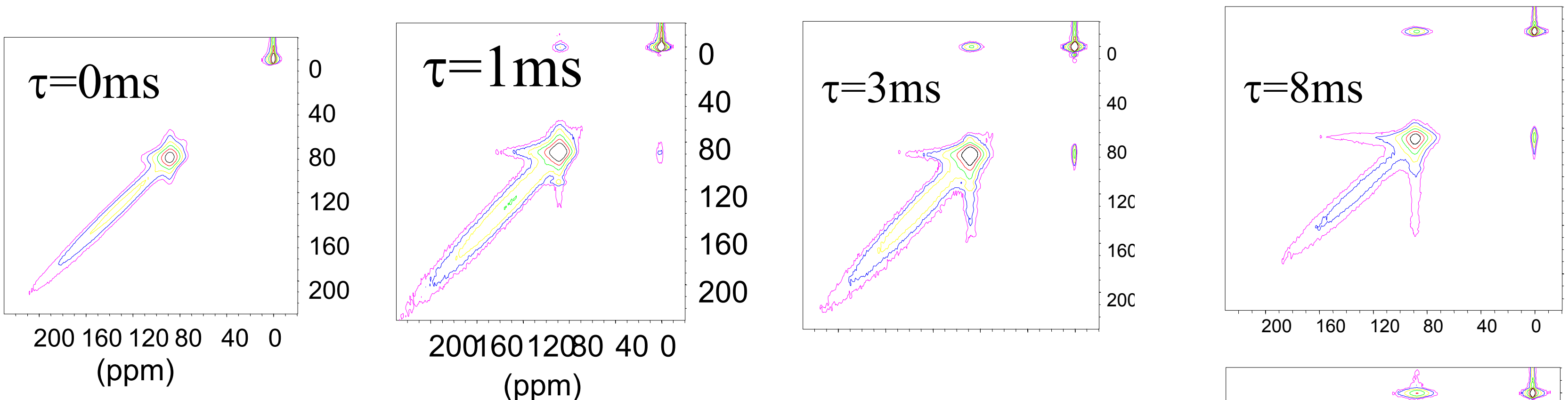


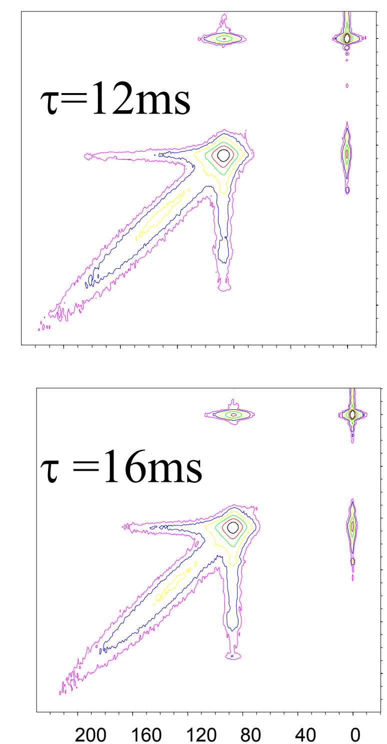
- The chemical shift data is fit to a phenomenological model of the xenon absorption process that takes into account:
  - Adsorption enthalpy (Δ H)
  - Henry's law constant (K_o)
  - Geometric parameter (η) (surface area to free volume ratio)
- η is a characteristic of the interconnectivity in free space
- The volume to surface ratio increases in proportion to R/C



Pore Connectivity Evaluated by 2D EXSY CF ^{129}Xe NMR

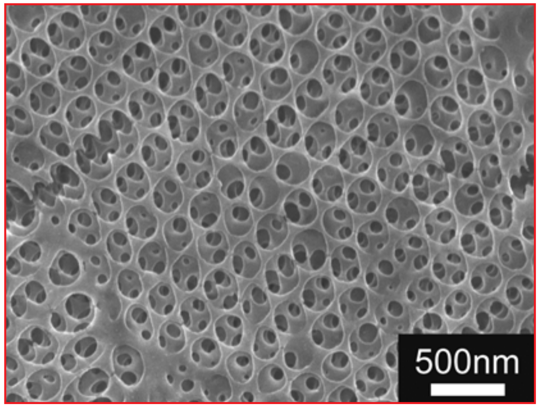
Spin exchange between regions of different chemical shift (different pores) is manifested by appearance of cross-peaks (non-diagonal elements)



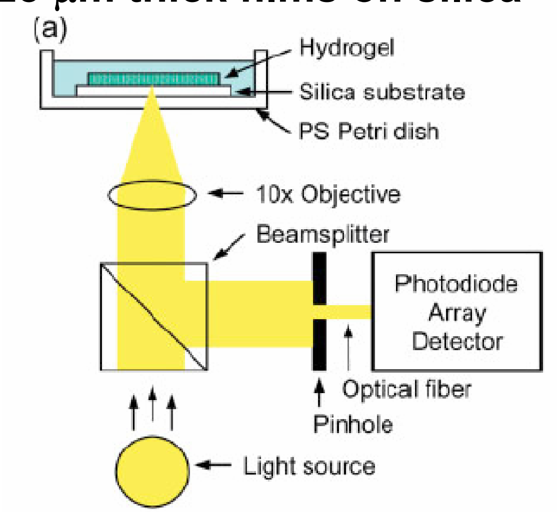


- **^{129}Xe spectra reveal two different resonance regions associated with micropores and macropores**
- **Exchange between mesopores and micropores is faster than between two micropores indicating short range connectivity**
- **Interconnectivity of pores correlates with processing parameters (R / C ratio)**

Tunable Inverse Opal Hydrogel pH Sensors

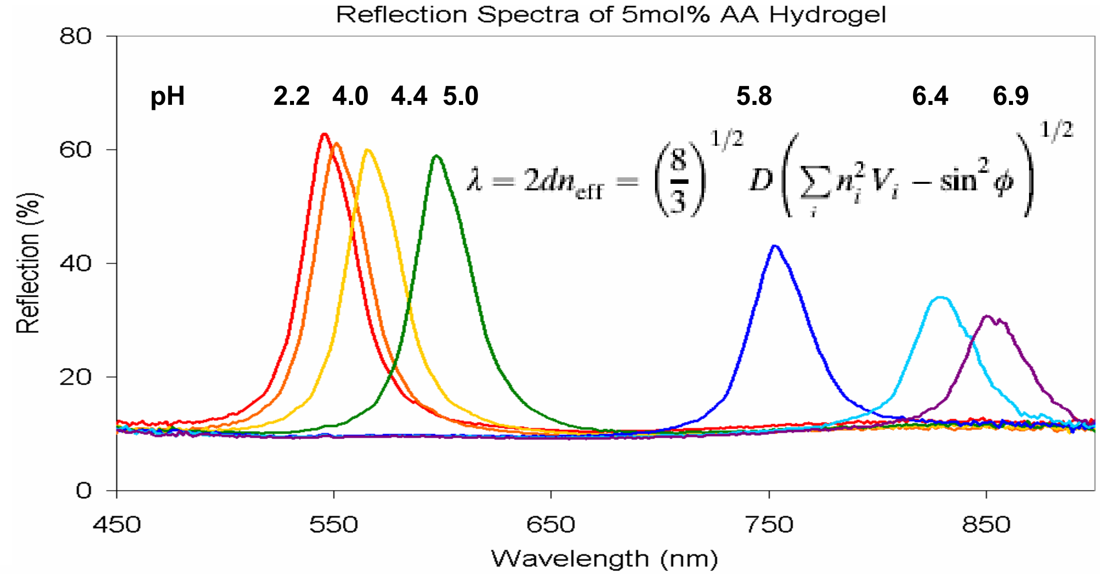


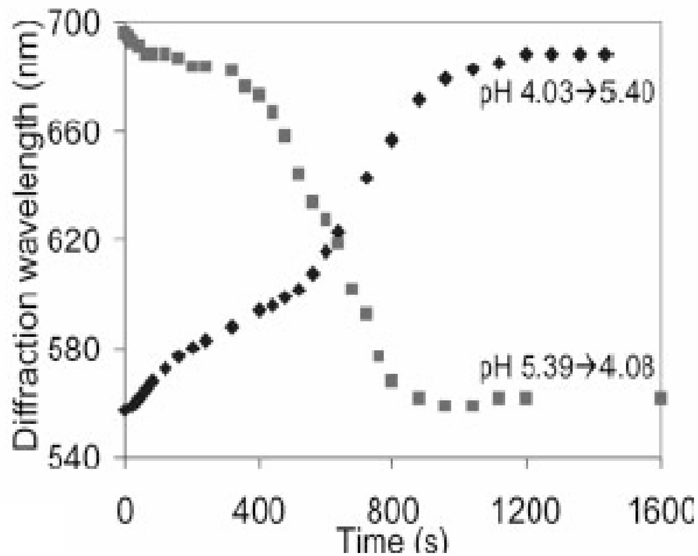
Use a colloidal crystal template appoach to grow 23 μm thick films on silica



Measure film reflectance in phosphate buffers.

Film color reversibly changes as a function of pH and ionic salt content of the solution.





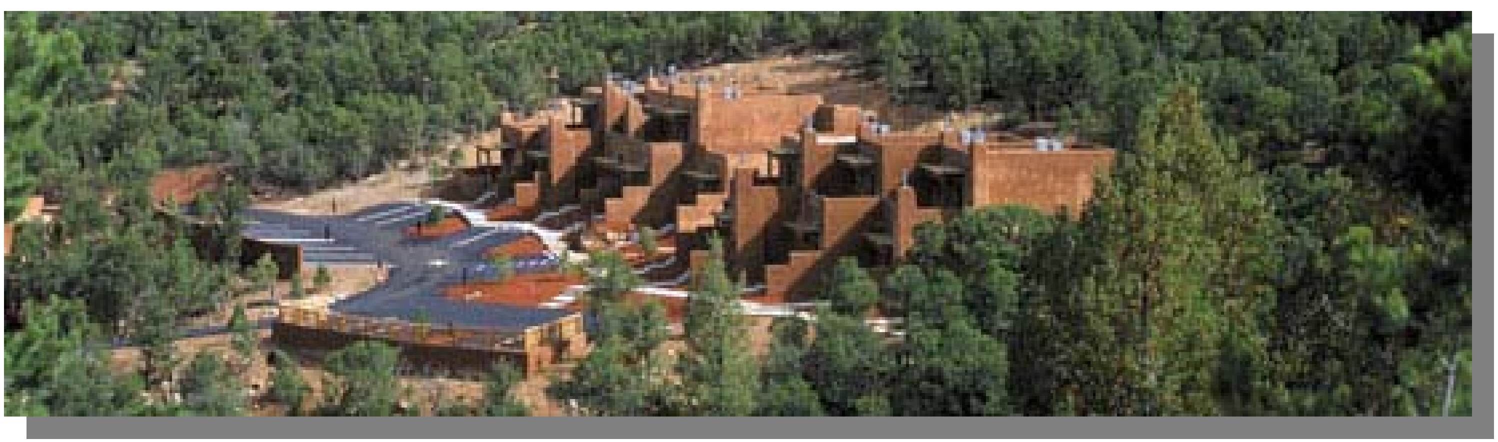
Ongoing efforts focus on accelerating and fine tuning the diffraction response by changing film dimensions and resident chemistry.

C
S
P

DOE/BES Workshop

Smart Materials Derived Through Molecular Assembly

Supported by
The Polymers task (Smart Materials Based on Electroactive Polymers)
DOE Center of Excellence
for the Synthesis and Processing of Advanced Materials
and
The Tailored Nanostructures task
Joint DP/BES NNI Network



Bishop’s Lodge, Sante Fe, NM
29 September - 1 October 2002

Organized by GJ Exarhos PNNL

Published Papers

- X-ray absorption studies of poly(vinylferrocene) polymers for anion separation, M. Balasubramanian, M.T. Giacomini, H. S. Lee, J. McBreen, and J. H. Sukamto, J *Electrochem. Soc.*, **149**, D137 (2002). **(BNL and PNNL)**
- Yongsoon Shin, Jun Liu, Jeong Ho Chang, Gregory J. Exarhos, "Sustained drug release on Temperature-Responsive poly(*N*-isopropylacrylamide)-Integrated Hydroxyapatite", Chem Commun 16: 1718 (2002). **(SNL and PNNL)**
- Igor L. Moudrakovski, VV Terskikh, CI Ratcliffe, JA Ripmeester, Li-Qiong Wang, Yongsoon Shin, and Gregory J. Exarhos. "A ^{129}Xe NMR Study of Functionalized Ordered Mesoporous Silica." *Journal of Physical Chemistry B* 106(23):5938-5946 (2002). **(PNNL and NRC)**
- Y. Sun, J.L. Qi, B.I. Lee, William D. Samuels, and Gregory J. Exarhos. "Preparation of Y_2O_3:Eu^{3+} Phosphors by a Urea Solvothermal Method." J. Am. Ceram. Soc., in review (2002). **(Clemson and PNNL)**
- G. Belomoin, E. Rogozhina, J. Therrien, P. V. Braun, L. Abuhassan, M. H. Nayfeh, L. Wagner, L. Mitas: Effects of surface termination on the band gap of ultrabright Si-29 nanoparticles: Experiments and computational models, *Physical Review B* **65**, 193406 (2002).
- O. M. Wilson, X. Hu, D. G. Cahill, and P. V. Braun: Colloidal metal particles as probes of nanoscale thermal transport in fluids, *Physical Review B* 66, 224301 (2002).
- S. Jeon and P. V. Braun: Hydrothermal synthesis of Er-doped luminescent TiO_2 nanoparticles, *Chemistry of Materials* **15**, 1256-1263 (2003).
- Y.-J. Lee and P. V. Braun: Tunable inverse opal hydrogel pH sensors, *Advanced Materials*, **15**, 563-566(2003).
- Jeong Ho Chang, Li-Qiong Wang, Yongsoon Shin, Beyongmoon Jeong, Jerry C. Birnbaum, and Gregory J. Exarhos. "The Core-Shell Approach to Formation of Ordered Nanoporous Materials." *Advanced Materials* 14(5): 378-382 (2002).
- Li-Qiong Wang, and Gregory J. Exarhos. "Investigation of Local Molecular Ordering in Layered Surfactant-silicate Mesophase Composites." *Journal of Physical Chemistry B* 223:U418-U419. (2002).
- Yongsoon Shin, Li-Qiong Wang, JeongHo Chang, William D. Samuels, Larry R. Pederson, and Gregory J. Exarhos. 2002. "Control of Hierarchically Ordered Positive and Negative Replicas of Wood Cellular Structures by Sol-Gel Mineralization." MRS Proceedings 726:72 (2002).
- Jeong Ho Chang, Yongsoon Shin, Li-Qiong Wang, and Gregory J. Exarhos. 2002. "Formation of Ordered Nanoporous Structure with Controlled Micelle Size." MRS Proceedings 733E:41 (2002).
- Li-Qiong Wang, Yongsoon. Shin, Gregory J. Exarhos, Igor L. Moudrakovski, V.V. Terskikh, C.I. Ratcliffe, and J.A. Ripmeester, "^{129}Xe NMR Study of Nanostructured Mesoporous Materials", To appear in J. Phys. Chem. A (2002).
- Yongsoon Shin, Li-Qiong Wang, JeongHo Chang, and Gregory J. Exarhos. 2002. "Morphology Control of Hierarchically Ordered Cellular Ceramic Materials Prepared by Surfactant-Directed Sol-Gel Mineralization of Wood Cellular Structures." In *Proceedings of IMMS 2002.*

Submitted Papers

- Liang Liang, Jun Liu, Charles F. Windisch, Jr., Yuehe Lin, and Gregory J. Exarhos, “Templateless Assembly of Large Arrays of Oriented Conducting Polymer Nanowires”, submitted to Mat. Lett. **(SNL and PNNL)**
- Y. Shin, L.-Q. Wang, J. Liu, G. J. Exarhos, “pH-Controlled Synthesis of Hierarchically Ordered Ceramics with Wood Cellular Structures by Surfactant-Directed Sol-Gel Procedure” *Journal Of Industrial and Engineering Chemistry* 2003, Submitted (Invited). **(SNL and PNNL)**
- Jun Liu, Liang Liang, Charles F. Windisch, Jr., Dale L. Huber, Gregory J.Exarhos, Yuehe Lin, “Templateless Assembly of Oriented Nanowires of Molecularly Aligned Conducting Polymers” submitted to Angewandte Chemie, International Edition, (2002). **(SNL and PNNL)**
- Jun Liu, Liang Liang, Charles F. Windisch, Jr., Gregory J. Exarhos, Yuehe Lin, “Templateless Assembly of Large Arrays of Oriented Conducting Polymer Nanowires”, submitted to Angewandte Chemie, International Edition (2003). **(SNL and PNNL)**
- Y. Shin, G. E. Fryxell, G. J. Exarhos, “Self-assembly of surfactants at the Interface of Air-Organic Salts”, Manuscript in preparation.
- Jeong Ho Chang, Yongsoon Shin, Young-Kook Shin, and Gregory J. Exarhos, “Catalysis of p-Nitrophenol Alkanoates on Self-Assembled Multifunctionalized Nanoporous Catalysts”, Accepted for publication and to appear in Chem. Comm. (2003)
- P. V. Braun and P. Wiltzius: Macroporous materials – electrochemically grown photonic crystals, in press, *Advances in Colloid and Interface Science* (2002).
- C.J. Orme, M.K. Harrup, J.D. McCoy, D.H. Weinkauf, F.F. Stewart, "Pervaporation of Water-Dye, Alcohol-Dye, and Water-Alcohol Mixtures Using a Polyphosphazene Membrane", *J. Membrane Sci.* Submitted for Publication.
- Thomas A. Luther, Frederick F. Stewart, Robert P. Lash, John E. Wey, and Mason K. Harrup, "Synthesis and Characterization of Poly[hexakis((methyl)(4-hydroxyphenoxy))cyclotriphosphazene]," *Journal of Applied Polymer Science*, In Press.
- D. L. Huber, J. G. Kushmerick, T. D. Dunbar, M. J. Samara, C. Matzke, R. Manginell, and B. C. Bunker, “Reversible Adsorption of Proteins onto a Thermally Switchable Monolayer” – in preparation for Langmuir

University Interactions

- University of Minnesota, Frank Bates - Joint Project with ORNL, *Designer Nanoscale Materials from Self-Assembly of Tri-Block Copolymers*; and NSET proposal development, *Integrated Design of nanostructured Multi-Block Copolymer Materials*
- University of California, Santa Barbara, Glenn Friedrickson, joint proposal development with ORNL
- SNL and Brian Salvatore at U South Carolina, *Synthesis of Polypeptides for Tethering to Self-Assembled Monolayers*
- Joint BNL/PNNL/U Minnesota DOE-EM project, *Electrically Conductive Polymers for Cleaning up Nuclear Waste*
- Collaborative activities with University groups promoted by the Center Project – Montana State University, *Platinum Nanowires Project*. Staff involved – Professors Edwin Abbott and Lee Spangler, Graduate student Bernard Anderson, Undergraduate students Colin Ingram, and Travis Bridges.
- University of California-Santa Barbara - Galen Stukey and Jennifer Cha, and PNNL, *True Cooperative Assembly of Composite Materials Using Polypeptides*
- SUNY Stony Brook and BNL - C. Grey, B. Hsaio; NMR studies of $LiMn_2O_4$, electrospun polymers
- We have growing interactions with Prof. Pierre Wiltzius. Prof. Wiltzius was at Bell Labs until about 1 year ago, and is now on the faculty at UIUC. We also interact regularly with Profs. Jennifer Lewis (FS-MRL, UIUC) and Gerard Wong (FS-MRL, UIUC). We also are a finalist for an STC on water purification from the NSF; university partners include Ron Shen and others from Berkeley, as well as faculty of other institutions. UI/MRL
- Prof. Luping Yu and Hengbin Wang, University of Chicago, Department of Chemistry. AL
- Participant in the NSF Nanoscience Center at (NSEC) located at the Northwestern University. ANL
- Collaboratiive research has been initiated with B. Hsaio and B. Chu of SUNY Stony Brook on the application of electrospun polymers to develop functional nanomaterials for batteries and fuel cells. BL
- SUNY Stony Brook - C. Grey, Solid State NMR
- SUNY Stony Brook - B. Hsaio, and B. Chu, Electrospun Polymers
- Waseda University – H. Nishide, Polymers for Oxygen Transpo
- University of Sao Paulo, Sao Carlos – E. A. Ticianelli, ElectricallyConducting Polymer Catalyst Supports
- University of Florida, Professor Paul Holloway, Optical limiting
- Washington State University, Professor Yogendra Gupta, Charge Transport and OLED materials

Program Leveraging with other DOE Offices

- New EE work likely on stable electrolytes for lithium-ion batteries for hybrid electric vehicles (BNL)
- Molecular composites for subsurface barriers (EM), EE funds for high energy power source needs
- Joint BNL/PNNL/U Minnesota DOE-EM project on electrically conductive polymers for cleaning up nuclear waste
- PNNL and BNL; XAS studies of polymers for separation of technetium from nitrate in nuclear wastes
- Perm-selective membranes for separations (EE and EM)
  - Chromatography packing material
  - Variable permeability membranes
- Periodic dielectric for photonic bandgap materials applications (EE)
- Ferroelectric and electrostrictive materials used for energy-conversion applications (artificial muscles)
- Electroactive Polymers for chemical motors
- Smart skins invoking a dimensional change for actuation of a control surface
- Stimulated color change in clothes or fabrics
- Polymer Light-Emitting Devices and Displays
- Advanced Lighting Initiative
- NNSA, Defense Programs, Campaign 2

Selected Industry Collaborations

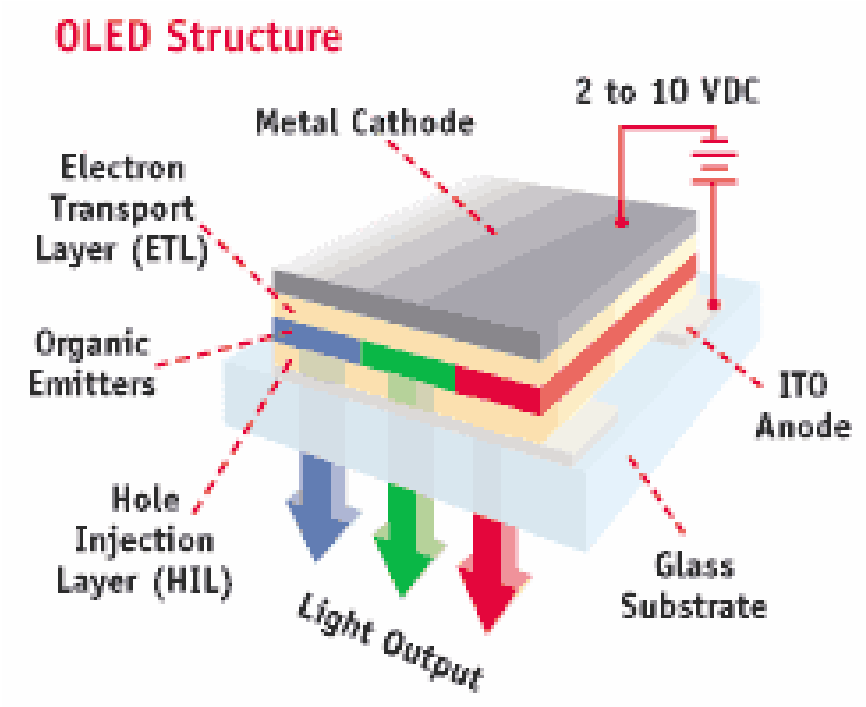
- Dow Chemical Company, Steven Hahn, joint proposal development with NSET
- Union carbide corp. and Ames on molecular engineering of polymer interfaces to promote adhesion
- Motorola with UI/MRL to see whether microperiodic electropolymerized materials have potential as actuators and capacitors
- BNL Subcontract with Technochem Co. on Phase II SBIR
- CRADA with Power Conversion, Inc. & BNL
- CRADA with Gould Electronics, Inc. & BNL
- Collaborative activities with industry related groups promoted by the Center Project - Discussions have been held with OPTEC of Montana State University and their industrial partners with a joint proposal submitted to Office of Science regarding synthesis and optical property characterization
- FMC Corp.- Y. Gao; XRD studies of lithium-ion battery cathode materials and BNL
- 3M Corp - R. Atanasoski; XAS on lithium polymer batteries and fuel cell electrocatalysts with BNL
- Gould Electronics, Inc. - M. L. Daroux, X. K. Xing; CRADA on XAS evaluation of lithium-ion battery cathodes and electrolyte additives (BNL)
- Power Conversion, Inc. - J. Drass; CRADA on thin film Lithium batteries (BNL)
- Motorola has committed funding (1 graduate student) in part to study if templated microperiodic electropolymerized materials have potential as actuators and supercapacitors.
- A CRADA with Gould Electronics, Inc. on electrolyte additives and study of cathodes was recently completed. This resulted in the development of *in situ* high-resolution XRD techniques to study cathode materials for lithium batteries. This led to the discovery of phase formations, during cycling of $LiMn_2O_4$, $LiCoO_2$ and $LiNiO_2$, that were not hitherto observed using conventional x-ray sources. At present we have a DOE EE project in conjunction with 3M Corp. It involves characterization of new alloy electrocatalysts on novel polymer supports. ANL
- Biomass Biorefinery for Production of Polymers and Fuel" DOE OIT/IOF, $14M 50/50 project with Metabolix, Inc., FY02-06, funded

Program Leveraging Activities

- Soft matter materials science and block copolymer studies pursued in this Center project were featured in a $ 40M proposal to DOE/BES *Center for Nanophase Materials Sciences* at ORNL recently funded
- *Cooperative Phenomena in Molecular Nanocomposites* funded at Sandia by the Division of Materials Science, Office of Basic Energy Sciences
- Polymer Materials Program at INEEL
- National Science Foundation Materials Science/Nanomaterials Initiative
- DOE-Office of Science Nano-Science/Materials Initiative
- Joint DP/DOE NanoScience and Technology Program - Project entitled, *Design and Synthesis of Tailored Nanostructures* (PNNL,LANL, SNL, ANL, LLNL)
- DARPA, *Electroactive Polymers Program*, PNNL
- ONR, *Charge Migration Across Solid-Solid Interfaces*, PNNL, WSU

Interactions with Other Labs

- **Through LDRD funding from Sandia National Lab (Paul Clem and Nelson Bell), we are investigating new nanophotonic materials which include studying the use of our electropolymerized three-dimensionally microperiodic structure as reactive photonic crystals. UI/MRL**
- **As part of our recently awarded NSF Nanoscience and Engineering Center on the Directed Assembly of Nanostructures we are collaborating with several theorists at LANL UI/MRL**
- **As part of our proposed STC on water purification, we are collaborating with Eric Peterson (INEEL) on polymer membrane synthesis and characterization.UI/MRL**
- **Because of our work on XAS of conducting polymers on our BES program we were asked to collaborate with PNNL (T. Hubler) on a DOE-EM program on the use of conductive polymers in nuclear waste cleanup. This program has recently been renewed for another three years. A paper on this joint effort has recently been accepted for publication. BNL**


OLED Structure
2 to 10 VDC
Metal Cathode
Electron Transport Layer (ETL)
Organic Emitters
ITO Anode
Hole Injection Layer (HIL)
Glass Substrate
Light Output